Underetching from simple stochastic etching kinetics

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The morphological richness of electrochemical semiconductor etching is not sufficiently counterparted yet by theoretical modeling. This paper investigates a minimal version of the Current-Burst model with Aging of Föll and Carstensen and demonstrates for a restricted geometry that the Aging concept is essential for underetching, or cavity generation. If the influence of Aging is neglected, the dynamics reduces to a Random Etching Model similar to the Random Deposition model. This computer *gedanken experiment* demonstrates that the stochastic dynamics with ageing-dependent kinetic reaction probabilities accounts for the different etching morphologies compared to those obtained in surface roughening and related systems.

The electrochemical semiconductor-electrolyte interface shows various types of highly nonlinear and non-equilibrium phenomena. Various reasons come into play: First, any chemical reaction — if not well stirred — is a nonlinear and spatial dynamical system as the reaction rates are a product of at least two reactand densities. Second, most etching systems, especially in production systems, are driven with a high current density, resulting in a far-from-equilibrium situation. Third, local clustering of etching activity is energetically favorable to a homogeneous density, resulting in cooperative phenomena and synchronization. Fourth, hydrodynamic and diffusion limitations delimit reaction rates. The interplay between nonlinear kinetics and e.g. diffusion limitation gives rise to rich spatio-temporal pattern formation. Reaction-diffusion systems have been studied widely and model various inhomogeneous modes of pattern formation as travelling waves, solitonic structures, and spiral waves, and been widely applied to catalytic reactions. Yet the morphology of the surface remains unchanged. For etching, or corrosion, the surface atoms are not inert as in catalysis, but themselves take part in the reaction dynamics. In addition that morphology is modified according to local concentrations, also the morphology influences the concentrations.

Current-Burst Model with Aging The Current-Burst (CB) model developed by Föll and Carstensen [1, 2] explains qualitatively a large variety of semiconductor etching experiments from a stochastic nonequilibrium dynamics based on very few assumptions. Due to the large range of scales involved in space and time, neither ab initio methods nor a full 3D simulation with CB size evolution are computationally feasible if one wants to explain e.g. branching morphologies and their open-loop control suppression [3] or even fractal structures [4, 5, 6]. The qualitative understanding has developed quite far to a detailed understanding of the different morphologies in different types of semiconductors (n/p type, Si, Ge, II/V-compounds), different etchants (HF, organic) and different parameters (front/backside illumination, doping level, temperature, current amplitude and waveform).

The Current Burst Model can be defined as follows. Etching, i.e. the dissolution of semiconductor atoms, occurs only within *bursting* events localized both in time and space, a typical size can be 10^3 atoms. The CB is an irreversible process far from equilibrium with initially high energy dissipation density; local

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high electrical field strength induces cracks within a characteristic radius, along those, atoms are dissoluted on a short time scale.

New etching events are initialized where surface passivation e.g. by hydrogen is absent, i.e. unsaturated binding valences are present. Their density is highest immediately after the etching event, differs for the different surface orientations in which a disordered surface dominatly facets (e.g. $< 100 >$ and $< 111 >$ in Si) and decreases exponentially with time, with different time constants for the surface orientations. As a consequence, the initialization density of events, which depends linearly on the density of available bonds, itself decreases exponentially with time, until it saturates to a very low probability density similar to that of the inert surface.

In the stochastic picture, these kinetic reaction rates take the role of reaction probabilities. Hereby the corresponding kinetic Monte Carlo model is defined; the experimental default setup of galvanostatic etching is straightforwardly modeled by a normalization of the field of local reaction probabilities over all surface elements.

In a fully detailed model, the electric potential within the bulk, diffusion limitations, the electrochemic double layer etc. should be taken into account. This is neglected within the model presented here; not aiming at an exact morphology prediction, but demonstrating the difference to reaction kinetics as known in surface growth and surface roughening.

Minimal CB model in a 2D cross section Experimentally pore morphologies are analyzed by breaking the wafer and investigating the cleavage plane with a light or electron microscope — no in situ imaging technique is applicable during the etching. Thus experimental morphologies are available only for those cross-sections. Consequently, the three-dimensional arrangement of pores may be neglected in a first simplified model, i.e. a 2D cross section is studied. Once the 2D system is fully understood, the more complicated and computationally costly 3D case can be addressed also.

The minimal model is defined on a orthogonal lattice, and consists of cells or plaquettes (of the size ranging from one atom to one CB) being occupied (1) or empty (0). Every bond between a 1 cell and a 0 cell corresponds to a surface element.

The minimal model is implemented by a kinetic Monte-Carlo simulation where each surface element has a local memory of the time where it became a surface element. Then CB's are initialized according to both the field of local reaction probabilities and the pre-set current density (of plaquettes per time step). Each element that is chosen for reaction in the Monte Carlo process initiates dissolution of all cells within a certain radius. In the simulations presented here, a minimal size of CB's is used (of radius 1/2),[1] and the CB model is studied with istotropeous aging under galvanostatic conditions.

Results. 1. The system shows strong underetching and readily generates cavities, as shown in Fig. 1. Due to the geometric artefact, etching in $< 11 >$ direction is favored, contrary to the situation in Si, where the $< 10 >$ direction etches dominantly. Thus straight-wall pore geometries are not obtained within this model.

2. Comparison to a "Random Aggregation" (or Etching) Model If all kinetic rates are set to a homogeneous and time-independent constant, the morphology creating effect of *space-time correlations* of CB's due to the aging must vanish; therefore only disordered etching is expected. This effect demonstrates easily, as shown in Fig. 2, no other parameters have beein changed.

[1] Nota bene *this implementation* bears "geometric artefacts", thus is not expected to predict the exact spatial structure. Here $< 11 >$ model surfaces have compared to $< 10 >$ model surfaces a factor$\sqrt{2}$ higher density of surface elements, contrary to a factor 1 in the real system. This leads to favored etching in $< 11 >$ direction contrary to the situation in Si, where the $< 10 >$ direction is preferred in etching. In a refined model, this could be corrected in the model by a rescaling of the ratio of the passivation time constants.

If all kinetic rates are equal, the model corresponds to an isotropic ("non-MBE") version of Random Deposition Model, or "not-diffusion-limited" DLA. — While the RD model, the Eden model, DLA and other variants have been studied extensively (see [7] for a review and introduction of scaling concepts in surface growth), this (isotropic-deposition) random aggregation (or etching) model seems to be less studied, e.g. it should be clarified to which universality class it belongs and which scaling exponents describe the surface roughening in this model.

Fig. 1 Kinetic Monte Carlo simulation of the Current-Burst Model with Aging. The system shows strong underetching and readily generates cavities. Here 250 cells with periodic boundary conditions are used.

Fig. 2 Random Etching (or Random Aggregation) Model: Uncorrelated stochastic etching, resulting in surface roughening. Underetching is possible, but occurs rarely.

Discussion and Outlook The model investigated shows that the locally time-dependent dynamics resulting from the aging concept introduces geometries dramatically different from those known from surface roughening: Underetching of cavities is favored, and inert sites remain unattached for a long period. This behavior is absent in known models of surface roughening. If aging effects are switched off in the simulation, surface roughening kinetics is restored. This model thus provides a "test plant" to check theoretically the effect of switched-on/off aging. Apart from this qualitative result, the different aging kinetics for each surface orientation should be included as well as Current Burst sizes of more than one lattice constant should be taken into account. This will be subject of further investigation.

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